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(NASA-TM-104526) IMPEDANCES OF Li/SO2 CELLS RETRIEVED FROM THE LONG DURATION EXPOSURE FACILITY (LDEF SATELLITE) AND COMPARISON WITH CELLS STORED TERRESTRIALLY (NASA) 9 p CSCL 10A

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IMPEDANCES OF Li/SO_2 CELLS RETRIEVED FROM THE LONG DURATION EXPOSURE FACILITY (LDEF SATELLITE) AND COMPARISON WITH CELLS STORED TERRESTRIALLY

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SUMMARY

Impedances have been measured on several Li/SO_2 cells retrieved from the LDEF satellite. These cells had been used to power instruments and recorders and had all been partially or fully discharged. Impedances were also measured on several cells that had been stored in cold storage since manufacture. Unfortunately, none of the cells stored terrestrially had undergone any discharge, whereas all of the cells on the satellite had been at least partially discharged early in the mission and then remained on orbit for about 5 years further. It has been observed by others that storage of a Li/SO_2 cell after partial discharge increases the resistance and thickness of the passive film on the Li electrode, as indicated by an increase in the time for recovery of voltage when a load is applied (voltage lag), or in some cases by an inability of a cell to sustain a normal current after such storage. Since the cells stored terrestrially had not been discharged in the same manner as the LDEF cells, a direct comparison cannot be made. Thus the effects of the space environment cannot be separated from the effects of storage after partial discharge. It is believed that the increases in impedance in the LDEF cells are largely due to the storage upon partial discharge rather than the effects of the space environment.

EXPERIMENTAL

The LDEF satellite contained about 95 batteries, of which 18 were sent to the Naval Weapons Support Center, Crane, IN for impedance tests and for characterization by means of discharge tests and DPA. The impedance experiments were carried out at the Lithium Battery Destructive Test Facility.

The batteries had been made in about 1985 from D-size Li/SO_2 cells, type LO-26S-22, manufactured by Mallory Battery Co., now Duracell. They were arranged in three different configurations with voltages of 7.5 V (12 cells in four parallel three-cell strings), 12 V (10 cells in two parallel five-cell strings) or 28 V (11 cells in series). The cells contained about 20 percent excess SO_2. Nominal capacity when manufactured was 7.0 AH.

Three of the batteries were dismantled, and impedance measurements made on individual cells from these batteries. The equipment consisted of a Solartron 1250 Frequency Response Analyzer, a 1286 Electrochemical Interface, and associated computer and plotter. Measurements were made from 10 000 to 0.00631 Hz with a root-mean-square ac signal of 1 mV (2.82 mV peak-to-peak voltage).

RESULTS AND DISCUSSION

The first cell studied was cell number 2 from Battery F070 used on the Solar Photovoltaic Experiment. The battery and all cells were completely discharged. There was a great deal of scatter in the measurements, and the impedance was very large (fig. 1) as would be expected for a discharged cell.

The second battery (F067 from the Space Effects Experiment) was at a nominal state of charge of 76 percent, based on the capacity estimated to have been withdrawn while in orbit. The open circuit voltages were all within a few millivolts of 3.000 V. Impedances of three cells were measured. Again there was much scatter. Impedances of cells number 5 and 6 were almost identical, that of cell number 1 was somewhat lower (figs. 2 and 3). Cell number 1 was discharged in order to determine the residual capacity. At the initial 2 A current the voltage went negative. The current was reduced to 1.5 A for 20 min; during this time the voltage remained negative. The current was reduced briefly to 200 mA and the voltage became positive. A 100 mA discharge was used for 20 min, during which the voltage increased due to breakdown of the passive film on the anode. The current was then increased to 200 mA for 5 min without significant voltage loss. A final discharge current of 500 mA was used. A total of only 0.633 AH for all the combined discharge steps was withdrawn before the voltage fell to zero. Based on the results with the unused cell which had been kept in cold storage terrestrially, the cell was at an actual SOC of about 9 percent. This series of measurements illustrate the effects of the buildup of a secondary passive film on partially discharged electrodes and its breakdown during discharge which has been described earlier (refs. 1 and 3). Only relatively small currents could be withdrawn initially, but the breakdown of the secondary film allows successively larger amounts of current to be withdrawn during discharge without reversal of the cell voltage. It is possible that the residual capacity of the cell was actually somewhat greater than 9 percent if there was still a substantial amount of the secondary passive film on the electrode. DPA of some of these cells will be done at Crane, and it may be possible to determine whether the low capacity was due to the remains of the highly resistive secondary passive film on the anode or to the self-discharge of most of the remaining Li during the 6 years in space. Discharge curves are shown in figure 4.

The third battery studied (F116) was made from the same lot of cells and had been in cold storage at Langley Research Center from the time the batteries were manufactured. In a string of six cells, the voltages of the four center cells were 2.997$\pm$0.002 V, those of the end cells were 2.933 and 2.956 V. The impedances of cells number 4 and 5 were measured and were almost identical (figs. 5 and 6). Cell number 4 was discharged at 1.5 A for 20 min, then at 2 A for 60 min for a total of 2.5 AH withdrawn. The impedance was then measured. A second discharge step of 2.5 AH was carried out at 2 A for 1.25 hr the impedance measured again. A final discharge was carried out at 2 A to load voltages of 2.0 and 1.0 V. The final capacity to 2.0 V was 6.67 and 7.0 AH to 1.0 V. In addition to the impedance measurements before discharge and immediately after each discharge step, the impedance was measured after standing overnight after the first step. Figures 6 to 9 illustrate the decrease in the passive film impedance upon discharge and the increase upon standing overnight. The impedances after the second discharge step and after the final discharge are shown in figures 10 and 11, which illustrate the increase in impedance upon further discharge. In contrast to the partially discharged cells from the LDEF satellite, this undischarged cell which had been kept in cold storage could easily take a 2 A current drain without voltage reversal, although there was a certain amount of voltage delay as is shown in the discharge curves of figures 4(b) and (c). The nominal capacity of this type of cell after manufacture was 7.0 AH, thus all of the capacity was available after the 5-1/2 years of cold storage.

The estimated sums of the ohmic and kinetic resistances are given in table I. The resistances of the completely discharged cell is extremely large, probably because no Li metal remains. Those of the partially discharged cells are larger than those of the undischarged cell, consistent with results from other investigators (refs. 1 to 4) who have found that the thickness of the passive film on the Li is much greater in cells stored after partial discharge, that the voltage lag upon applying a load is much longer, and that often the current capability and capacity are considerably decreased.

The Warburg slopes are shown in table II. A larger slope indicates a slower rate of diffusion to the electrode. There is a fair amount of scatter, but in general, the slope is larger (i.e., the diffusion rate is slower) for the cells that have been in orbit after partial discharge. As discussed above, the passive layer on these cells is apparently thicker and more resistive than for fresh cells, so that the slower rate of diffusion would be expected.

Unfortunately, no conclusions can be drawn about the effects of the space environment because all of the batteries on LDEF had been discharged to some extent, and none of the batteries stored on Earth had been discharged at all. The effects observed are consistent with those observed by others on Li cells that have been stored after being partially discharged. It is felt that the differences that were observed between the LDEF cells and those stored on Earth are primarily due to the storage on orbit after partial discharge rather than any effects due to the space environment. It would have been useful to have had one or more of the batteries on Earth discharged in the same manner as one of those on LDEF, or alternatively, to have carried a cell on the LDEF satellite that did not undergo any discharge so that any differences could be unequivocally ascribed to the space environment.

The data do illustrate in an unambiguous manner that the impedance of the passive film falls when the cell is discharged, as has been postulated by others from the recovery of cell voltage after the initial discharge (i.e., the "voltage delay" phenomenon), and that the film impedance increases upon standing, especially with partially discharged cells, confirming earlier results of other investigators.

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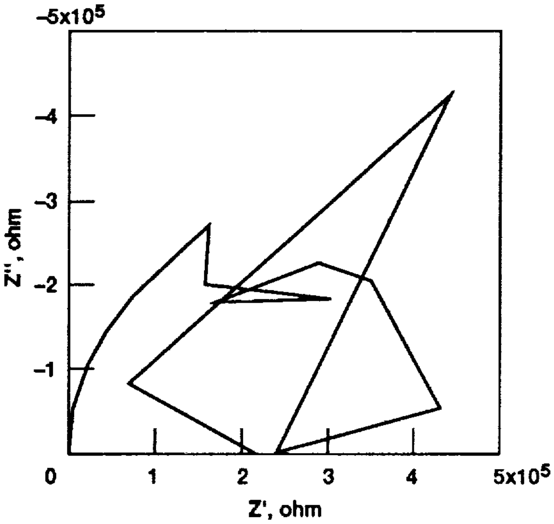


Figure 1.—Battery F070. Photovoltaic Experiment, 0% SOC. Impedance of cell #2, OCV = 0.080 V. Note scatter at low frequencies.

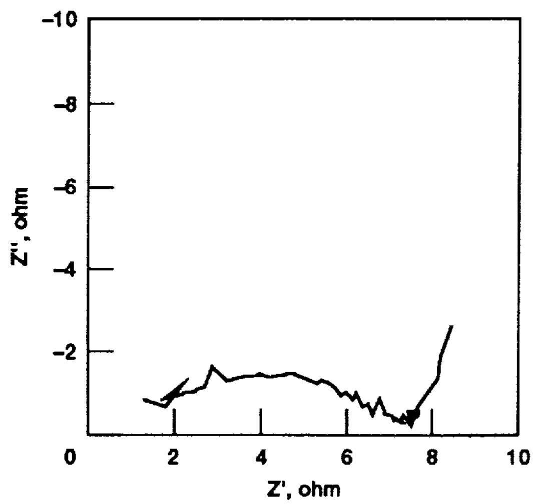


Figure 2.—Battery F067. Space Effects Experiment. Calculated SOC = 76%, experimental SOC = 9%. Impedance of cell #6, OCV = 3.000 V. (Cell #5 almost identical).

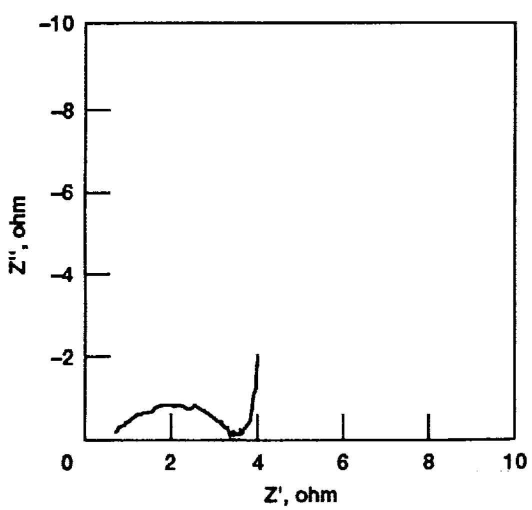
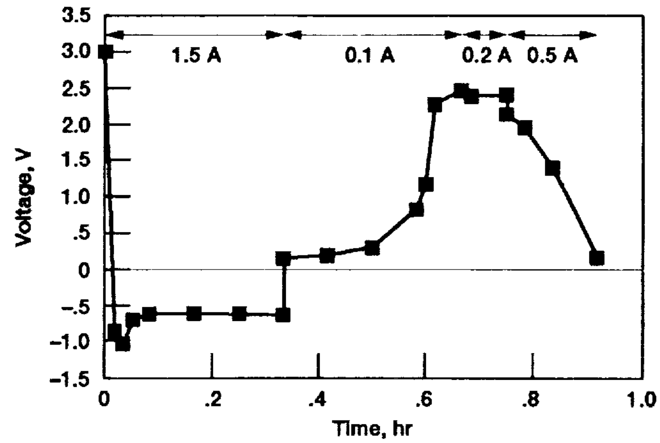
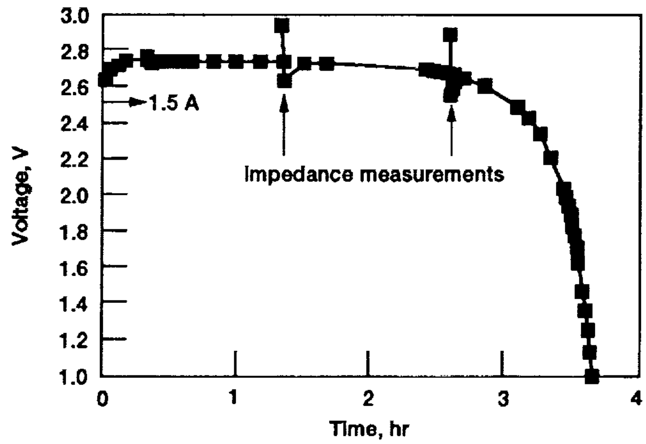


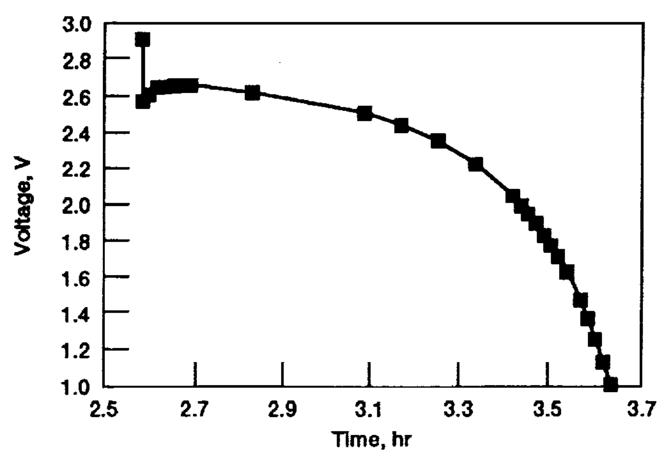
Figure 3.—Battery F067, Space Effects Experiments. Impedance of cell #1, OCV = 3.000 V.



(a) Battery F067. Discharge of cell #1, currents as shown. SOC by comparison of capacity to that of cell from unused battery F116 is 9%.



(b) Battery F116. Discharge of cell #4 at 2 A except first 20 minutes, as indicated. Impedance measured after 2.5 and 5.0 AH and discharge to 1.0 V. Note voltage lag (voltage drop followed by recovery) at start of discharge and at resumption of discharge after halt for impedance measurements.



(c) Expanded figure 4(b) showing last portion of discharge.

Figure 4.—Comparison of discharge curves for battery F067 and unused battery F116.

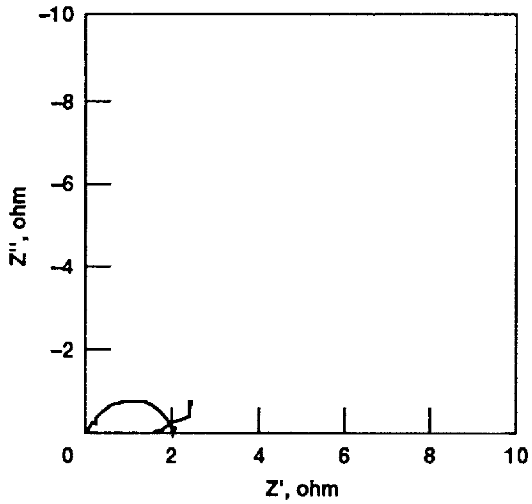


Figure 5.—Battery F116. Impedance of cell #5, OCV = 3.000 V.

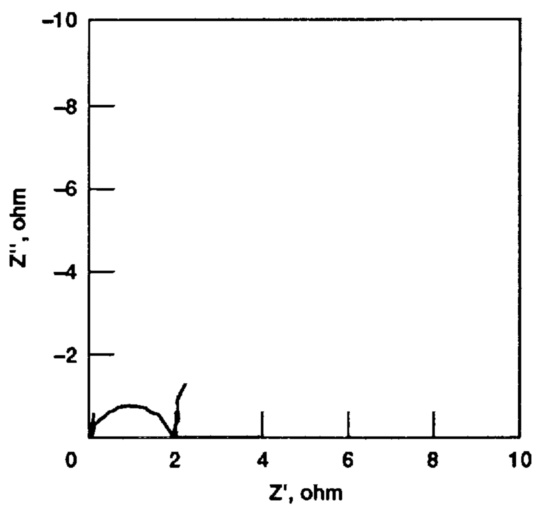


Figure 6.—Battery F116. Impedance of cell #4, OCV = 3.000 V.

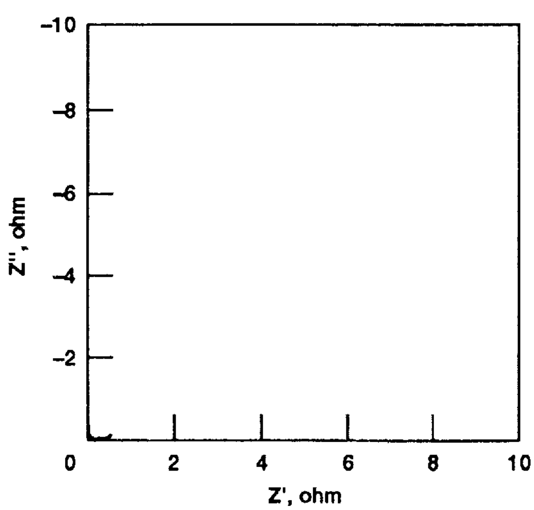


Figure 7.—As above, immediately after 2.5 AH discharge, OCV = 2.910. Same scale as Figure 5 and 6 to illustrate drop in impedance immediately after partial discharge.

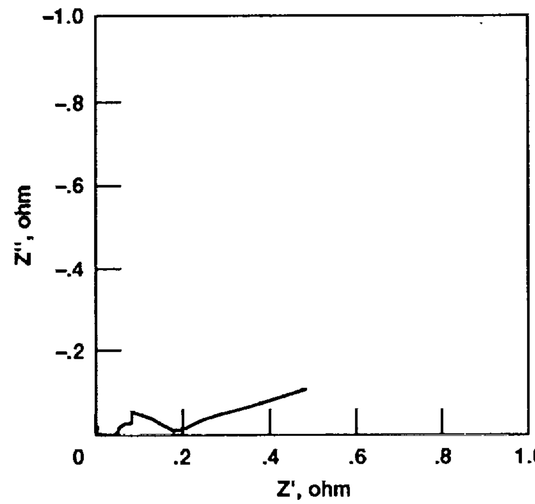


Figure 8.— As above but scale 10 x that of Figures 5-7.

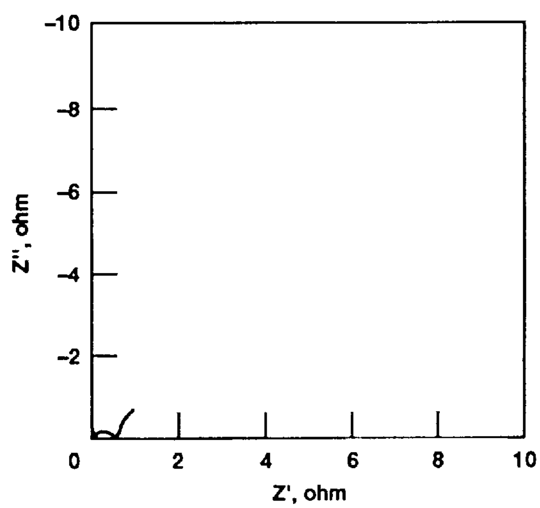


Figure 9.—As above, after standing 16 hr to illustrate increase of impedance upon standing after partial discharge. Same scale as Figures 5-7.

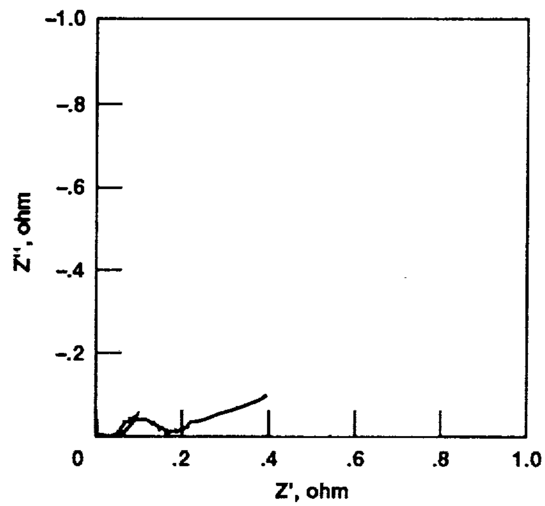


Figure 10.—As above, after second 2.5 AH discharge. Same sale as Figure 8 (10 x scale of Figures 5-7 and 9).

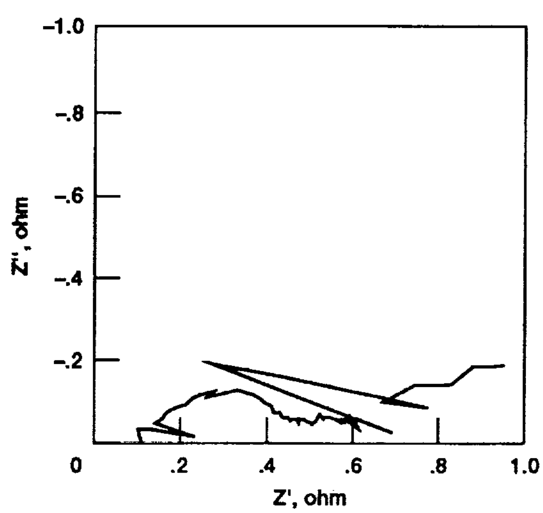


Figure 11.—As above, after discharge to 1.0 V. Same scale as Figures 5-7, 9 and 10. Note scatter due to depletion of anode.

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16. Abstract

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